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The Conductivity, Temperature Coefficients
of Conductivity, and Dissociation of Cer-
tain Electrolytes in Aqueous Solution
from 0° to 35°. Probable Induc-
tive Action in Solution, and
Evidence for the Com-
plexity of the Ion.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY



BY

LULA GAINES WINSTON.

BALTIMORE

June, 1911

EASTON, PA.:
ESCHENBACH PRINTING CO.
1911

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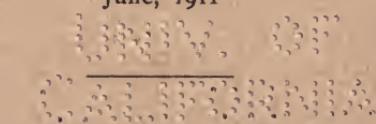
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TO HALL
AUDITION

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The Conductivity, Temperature Coefficients of Conductivity and Dissociation of Certain Electrolytes in Aqueous Solution from 0° to 35°.

Probable Inductive Action in Solution, and Evidence for the Complexity of the Ion.

INTRODUCTION

This paper forms one of a series dealing with the conductivity of electrolytes in aqueous solution. In it we shall take up for consideration the conductivity, temperature coefficients of conductivity, and percentage dissociation of certain salts, and shall show how these results confirm those already obtained, and point out some new relations. The work is part of an investigation which has been carried on in this laboratory for a dozen years or more. The importance of such an investigation is obvious, since chemistry is a branch of the science of solutions, and one of the very best methods of studying solutions is the conductivity method.

HISTORICAL

Electrochemical theories were advanced as early as 1807 by Davy and by Berzelius. Berzelius was among the first to call attention to the electrically charged atom. Faraday appeared later, giving to the world the laws which bear his name. His work has stood the test of time. His law showing the relation between the quantity of electricity and amount of decomposition holds rigidly to-day, and in the light of the electron theory takes on a new meaning. In the years 1853 to 1859 Hittorf determined the relative velocities of the ions of many salts. He pointed out a relation between chemical activity and conductivity, and also called attention to the analogy existing between solutions and gases. This latter problem was taken up later by Raoult, Ostwald, van't Hoff, and others. The laws of Raoult, dealing with the lowering of the freezing point and vapor pressure of liquids, and Ostwald's

dilution law are well known. Van't Hoff, in 1887, working on osmotic pressure, found certain solutions that behaved abnormally. Arrhenius, attempting to explain their behavior, pointed out the fact that salts and analogous substances break down into ions. Thus was given to the world the theory of electrolytic dissociation. Its truth is attested on every hand. Facts once inexplicable become wonderfully clear and lend confirmation to the theory. Many workers have appeared in the field since Arrhenius. The most important of these, perhaps, is Sir J. J. Thomson, whose brilliant experiments have well-nigh revolutionized our conception of matter.

The result of the work already done may be summarized briefly as follows: The conductivity of electrolytes in solution is dependent primarily on two things, viz., the number of ions and their velocity. These two factors may be affected by various others. The most important of these is temperature. The effect of rise in temperature is chiefly to increase the velocity of the ions. The number of ions would not be greatly affected unless they were complex. In addition to the effect of temperature on the number and velocity of ions in solution, there are still other factors which, for convenience, may be divided into three classes:

1. Those dependent upon the solute.
2. Those dependent upon the solvent.
3. Those dependent upon the combination of the solvent with the solute.

In class 1—factors dependent upon the solute—mention should be made first of all of the effect of valence. This would determine largely the number of ions capable of entering into solution. As is well known, the conductivities of binary, ternary and quaternary compounds are found to vary considerably. Factors affecting the velocity of the ion would be the atomic weights and atomic volumes of the elements existing in the compound. We would naturally expect that the velocity would be an inverse function of the atomic weight and atomic volume. Experimentally, however, this has not been found to be true. Jones and Pearce¹ found that those

¹ Am. Chem. J., 38, 737 (1907).

elements which have the smallest atomic volumes have the greatest hydrating power. This would tend to diminish their velocity.

As to the factors dependent upon the solvent, the most important are its viscosity, its dielectric constant and its association.

In class 3 should be placed the concentration of the solution and the power of the solute and solvent to form solvates with one another.

The conductivity of solutions has been studied from each of these standpoints, and much valuable data have been accumulated.

The effect of temperature has been worked out carefully by Jones and his coworkers, West,¹ Jacobson,² Clover,³ West,⁴ White,⁵ Wightman,⁶ and Hosford.⁷ Conductivity always increases with rise in temperature from 0° to 65° , while dissociation usually decreases slightly. The decrease in dissociation would tend to diminish the number of ions, and thus to lessen the conductivity, but this effect is more than offset by the increased velocity of the ions due to rise in temperature. This decrease in dissociation may be accounted for in two ways. It may be due to a decrease in the association of the solvent, which would tend to decrease the dissociation of the dissolved substance; or it may be due to the fact that a rise in temperature diminishes the dielectric constant of the solvent and consequently its dissociating power, since, according to the Thompson-Nernst hypothesis, a substance having a high dielectric constant has great dissociating power. While, as just shown, the effect of temperature is to diminish the number of ions present, its effect on the velocity of ions is just the reverse. Rise in temperature increases the velocity of ions in two ways: First, it diminishes the viscosity of the solvent. Second, rise in temperature would decrease the

¹ Am. Chem. J., **34**, 357 (1905).

² *Ibid.*, **40**, 355 (1908).

³ *Ibid.*, **43**, 187 (1910).

⁴ *Ibid.*, **44**, 508 (1910).

⁵ *Ibid.*, **44**, 159 (1910).

⁶ *Ibid.*, **46**, 56 (1911).

⁷ *Ibid.*, **46**, 240 (1911).

complexity of the hydrates formed. This also would tend to increase the velocity of the ions. At all events, the decrease in the number of ions seems to be more than compensated for by the increase in their velocity, and the general effect of rise in temperature is, therefore, to increase the conductivity.

The most important factor in its effect on conductivity with rise in temperature is hydration. That the dissolved substance combines with some of the solvent to form solvates seems now to be an undisputed fact, the existence of hydrates in solution being shown by several independent lines of evidence.¹ The close connection between hydration and water of crystallization has also been established in this laboratory.

Important relations between amount of hydration and temperature coefficients of conductivity have been pointed out. Jones and his coworkers, Bingham, McMaster, Rouiller,² Veazey,³ Guy,⁴ Davis, Reinhart, Mahin,⁵ Schmidt,⁶ and Kreider⁷ have made important observations on the effect of viscosity on the conductivity of electrolytes.

The work in this laboratory has been extended to non-aqueous solutions. Apparatus has been improved, the range of temperature has been extended, old sources of error have been eliminated, and the conductivities of hundreds of compounds have been added to those already measured.

The problem has been undertaken in this laboratory of *measuring the conductivity of all of the more common acids, bases and salts in aqueous solution, from 0° to 65°*, and of calculating the dissociation whenever possible.

This work will be pushed forward as rapidly and carefully as possible.

One fact, overlooked thus far in the consideration of the conductivity of electrolytes, is the probable inductive action⁸

¹ Publication No. 60 of the Carnegie Institution of Washington.

² Publication No. 80 of the Carnegie Institution of Washington.

³ Am. Chem. J., **41**, 433 (1909).

⁴ *Ibid.*, **46**, 131 (1911).

⁵ *Ibid.*, **41**, 433 (1909).

⁶ *Ibid.*, **42**, 37 (1909).

⁷ *Ibid.*, **45**, 282 (1911).

⁸ *Ibid.*, **45**, 547 (1911).

of the ion on the unionized molecule. In the solution of a salt there is every condition necessary for inductive action. There are the charged ions, the neutral molecules and the dielectric or solvent. Ordinary electrical induction in conductors, as is well known, takes place as follows: A charged body brought near to a neutral body, but separated from it by a dielectric, causes a separation of the electricity in the neutral body, drawing the opposite kind nearest to itself and repelling the like charge to the side farthest from itself. If, while the charged body is still near, the repelled charge in the conductor is removed by contact with some other body, on the removal of the charged body the once neutral body would be left charged with the opposite kind of electricity. The ion, a charged body, acting through the water (a dielectric) on an unionized molecule, would produce just such an effect. Several results may follow from this. First, a positive ion brought near to a neutral molecule, but separated from it by the nonconducting water, would cause a separation of the electricity in the molecule; the negative will be drawn near to the ion and the positive repelled. Suppose, for instance, that the repelled charge is not removed, the charged ion would simply attach itself to the molecule, and as a charged system move through the solution. Moreover, this charged system could play the part of the original ion and, acting through the water, in a similar way draw other molecules to itself. There would be a limit, of course, to the number of molecules which could thus be attached. This, no doubt, would be a function of the valency of the ion.

If, on the other hand, the repelled charge is removed and the inducing ion then moves off, the once neutral molecule would be left charged with a sign opposite to that on the inducing ion, and moving through the solution would be able to attract other molecules or oppositely charged ions to itself. This, of course, would give rise to a great complexity of ions and molecules. The velocity of the ions would thus be greatly affected, because their masses would be greatly increased. This may in a measure account for the apparent discrepancy between the dissociation as found by the freezing point method

and that found by conductivity, since by this inductive action there would be brought about a change in the number of particles which would probably affect the dissociation as found by the freezing point method.

The effect on conductivity, on the other hand, would be due rather to a change in the velocity of the ions. The complex ions would tend to move more slowly than the individual ion, thus making the conductivity measurements of dissociation too low. The change in the number of particles would not be so apparent in the case of conductivity because, when, by means of induction, an ion attaches itself to a neutral molecule, it would still give rise to a charged system, and would not thereby reduce the number of charged particles in solution. The breaking up of these moving systems by heat would show itself in increased temperature coefficients.

Jones and Pearce¹ have shown that the dissociation as measured by the conductivity method is less than that calculated from the freezing point lowering. Conditions were chosen such that the number of ions, velocity of ions, hydration and viscosity were the same in both cases. It was found by them that the greater the dilution, the greater the difference in dissociation as measured by the two methods. This is due to the fact that the complexity of the hydrate is greater, the greater the dilution.

Evidence seems to be accumulating in many directions that the ions in solution are complex. Some interesting relations are brought out in connection with the various dilution laws, to which sufficient attention has not as yet been directed, which apparently point to the complexity of molecules in solution. Ostwald's law,

$$\frac{\alpha^2}{(1-\alpha)V} = K$$

has been found to apply to weakly dissociated electrolytes, but not at all to strong electrolytes. Moreover, various dilution laws have been formulated which apply to strong electrolytes but are extremely unsatisfactory when it is attempted to apply them to weaker electrolytes.

¹ Am. Chem. J., 38, 743 (1907).

The question naturally arises, why this difference? The thought has suggested itself that it may be due to the complexity of the molecule—one dilution law applying to solutions containing molecules of a certain complexity, while another would apply to solutions containing molecules of a different order of complexity. Of the many dilution laws for strong electrolytes only two will be considered, viz., that of Rudolphi and that of Van't Hoff. The Rudolphi formula is

$$\frac{\alpha^2}{(1-\alpha)\sqrt{V}} = K$$

Van't Hoff's is

$$\frac{\alpha^3}{(1-\alpha)^2 V} = K$$

Since the Ostwald law,

$$\frac{\alpha^2}{(1-\alpha)V} = K$$

applies to weakly dissociated electrolytes, in solutions to which it applies there are very few ions. If the Rudolphi formula is applied to a solution, a certain volume, V_1 , is obtained, corresponding to a definite value for α and for K . If now, retaining the same values as before for α and for K , the Ostwald formula is applied to the same solution, there is obtained a volume V which is the square root of the volume obtained by the Rudolphi formula. In other words, there is found the relation $\sqrt{V_1}/V = 1$, a relation which would indicate complexity of the molecule in solutions to which the Rudolphi formula applies. Treating the Van't Hoff formula in the same way, i. e., comparing the volume obtained by the use of the Van't Hoff formula with a certain solution, for a definite value of α and of K , with the volume obtained by the use of the Ostwald formula for the same solution, keeping α and K the same as before, there is found the relation

$$\frac{V}{V_1} = \frac{1-\alpha}{\alpha}$$

where V represents the volume when the Ostwald law was applied and V_1 the volume obtained when the Van't Hoff law was used. Now if $V/V_1 = \text{constant}$, the molecular weight would be the same in each case; but on examining the formula it is

readily seen that the relation is not a constant one, but that it is a function of the dissociation. This would indicate complexity of the molecule in solutions to which the van't Hoff law applies. The interesting fact about this last relation is that the degree of complexity varies with the dissociation, i. e., with the number of ions present; just exactly what has been referred to above as the probable result of inductive action. Let us now turn to the consideration of the data in hand.

EXPERIMENTAL

The well known Kohlrausch method was used to determine the conductivities. A Kohlrausch slide wire bridge was employed with an induction coil and telephone receiver. The cells used were of the type designed by Jones and Bingham.¹ The cell constants were redetermined at regular, short intervals. The measurements were made at 0°, 12°.5, 25°, and 35°. Three separate readings were taken for each solution at each temperature, different resistances being used for each reading. The average of the conductivities obtained by using each of these readings was taken to be the correct conductivity.

The flasks and burettes were carefully calibrated at 20° by the method of Morse and Blalock.²

Solutions

Kahlbaum's "chemically pure" materials were taken as the starting point in almost every case. These were purified, whenever practicable, by crystallization. A solution somewhat more concentrated than the most concentrated solution to be used was made up. Its strength was determined by volumetric or gravimetric methods, and the solutions prepared from it as a mother solution. This solution was made by direct weighing whenever it was possible, and in the measurements given below this method was always used unless otherwise stated.

Water

The water used in making the solutions was prepared ac-

¹ Am. Chem. J., **34**, 493 (1903).

² *Ibid.*, **16**, 479 (1894).

cording to the method of Jones and Mackay,¹ which has been employed in this laboratory for many years. This method is too well known to need discussion here. The water thus obtained had a conductivity of about 0.9 to 1.3×10^{-6} at 0° .

Discussion of Results

The following salts have been classified, approximately, according to the position of the metal in the Periodic System. The ammonium, sodium and potassium compounds would, therefore, be first in order. These are, therefore, grouped together for consideration. A careful examination of the results for these compounds will show some points of interest.

(1) The difference in the conductivities of the binary, ternary and quaternary salts is quite evident. The conductivity of ammonium nitrate, potassium acetate, and potassium permanganate, between 0° and 35° , ranges from 46 at 0° , in the most concentrated solution of potassium acetate, to 163.62 at 35° in the most dilute solution of ammonium nitrate. The conductivity of those compounds which are not binary, viz., ammonium sulphate, acid ammonium sulphate, dipotassium phosphate, sodium sulphate, and borax, at 35° in the most dilute solutions is, in every case, above 200, and for acid ammonium sulphate is considerably above 500.

The very high values for the temperature coefficients of conductivity, expressed in conductivity units, in the case of the four sulphates is very noticeable. The highest values are 5, 6, and 7+ in the case of sodium sulphate, ammonium sulphate and acid ammonium sulphate, respectively; while for the other salts under consideration in this group, the temperature coefficient in conductivity units is 4+. This is probably due to the fact that sulphates show a tendency towards polymerization.

The very largest temperature coefficient of conductivity of this group belongs to acid ammonium sulphate. It is 7.96. This is doubtless accounted for by the fact that this salt breaks up into very complex ions.

In the case of potassium acetate and potassium perman-

¹ Am. Chem. J., 19, 91 (1897).

ganate, it is somewhat peculiar that the temperature coefficients of conductivity in per cent. are in both cases, from 0° through 25° , larger than those measured in conductivity units.

It is also striking that in the case of acid ammonium sulphate the temperature coefficients of conductivity decrease with rise in temperature.

In dealing with the following data the percentage dissociation is not discussed for the individual salts, but by means of curves which are given after the data their points of difference are brought out.

Ammonium Nitrate

Table I—Conductivity

<i>V</i>	0°	$12^{\circ}.5$	25°	35°
2	58.44	78.92	101.51	119.48
8	64.35	84.25	113.38	135.07
32	68.81	94.30	123.13	146.53
128	71.64	98.45	128.44	152.92
512	73.63	101.39	132.64	157.48
1024	74.69	102.51	134.43	159.44
2048	75.25	103.39	134.79	160.39
4096	76.37	105.51	137.87	163.62

Table II—Temperature Coefficients

<i>V</i>	0° - $12^{\circ}.5$		$12^{\circ}.5$ - 25°		25° - 35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.64	2.81	1.81	2.29	1.80	1.77
8	1.59	2.47	2.33	2.77	2.17	1.91
32	2.04	2.97	2.31	2.45	2.34	1.90
128	2.15	3.00	2.40	2.44	2.45	1.91
512	2.22	3.02	2.50	2.47	2.48	1.86
1024	2.23	2.99	2.55	2.49	2.50	1.86
2048	2.25	2.99	2.52	2.44	2.56	1.90
4096	2.33	3.05	2.59	2.46	2.58	1.87

Table III—Percentage Dissociation

<i>V</i>	0°	$12^{\circ}.5$	25°	35°
2	76.5	74.8	73.6	73.0
8	84.2	79.9	82.2	82.6
32	90.1	89.4	89.3	90.0
128	93.8	93.3	93.2	93.5
512	96.4	96.1	96.2	96.3
1024	97.8	97.2	97.5	97.5
2048	98.5	98.0	97.8	98.0
4096	100.0	100.0	100.0	100.0

*Ammonium Sulphate**Table IV—Conductivity*

<i>V</i>	0°	12°.5	25°	35°
2	82.37	112.09	145.09	170.72
8	98.06	136.28	179.57	213.19
32	115.27	160.26	210.98	254.86
128	130.95	182.65	241.38	291.69
512	139.69	195.77	259.21	313.00
1024	143.84	202.31	267.62	322.55
2048	150.62	209.74	275.96	337.47
4096	150.44	211.55	280.82	340.32

Table V—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	2.38	2.89	2.64	2.36	2.56	1.76
8	3.06	3.12	3.46	2.54	3.36	1.87
32	3.60	3.12	4.06	2.53	4.39	2.08
128	4.14	3.16	4.70	2.57	5.03	2.08
512	4.49	3.21	5.08	2.60	5.38	2.08
1024	4.68	3.25	5.22	2.58	5.49	2.05
2048	4.73	3.14	5.30	2.53	6.15	2.23
4096	4.89	3.25	5.54	2.58	5.95	2.12

Table VI—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
2	54.6	52.9	51.6	50.1
8	65.0	64.4	63.9	62.6
32	76.5	75.7	75.1	74.8
128	86.9	86.3	85.9	85.7
512	92.7	92.5	92.3	91.9
1024	95.4	95.6	95.2	94.7
2048	100.0	99.1	98.2	99.1
4096	99.8	100.0	100.0	100.0

*Acid Ammonium Sulphate**Table VII—Conductivity*

<i>V</i>	0°	12°.5	25°	35°
2	155.26	186.49	211.99	226.06
8	183.40	223.84	258.00	277.18
32	223.58	279.55	322.68	349.24
128	265.24	339.00	404.14	444.74
512	289.79	378.25	463.20	522.24
1024	295.22	386.88	483.51	547.05
2048	303.41	400.01	496.86	573.46
4096	304.26	401.96	497.11	576.66

Table VIII—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	2.50	1.61	2.04	1.09	1.41	0.66
8	4.04	2.20	2.73	1.22	1.91	0.74
32	4.48	2.00	3.45	1.23	2.66	0.82
128	5.90	2.22	5.21	1.54	4.06	1.01
512	7.08	2.44	6.79	1.80	5.90	1.27
1024	7.33	2.48	7.73	2.00	6.35	1.31
2048	7.73	2.55	7.74	1.94	7.66	1.54
4096	7.81	2.57	7.61	1.89	7.96	1.60

Table IX—Percentage Dissociation

V	0°	12°.5	25°	35°
2	51.0	46.4	42.7	39.2
8	60.3	55.7	51.9	48.1
32	73.5	69.6	65.0	60.6
128	87.1	84.4	81.3	77.1
512	95.2	94.2	93.2	90.5
1024	97.0	96.3	97.4	94.9
2048	99.7	99.6	99.9	99.4
4096	100.0	100.0	100.0	100.0

Sodium Sulphate

Table X—Conductivity

V	0°	12°.5	25°	35°
4	68.49	97.54	129.13	156.71
8	78.51	111.46	146.40	178.24
32	94.51	132.72	176.76	215.19
128	107.54	152.49	203.10	247.02
512	117.46	166.24	221.21	269.50
1024	119.65	169.61	226.34	276.92
2048	125.95	176.08	235.35	287.02
4096	127.73	181.61	243.42	294.48

Table XI—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.32	3.39	2.53	2.59	2.76	2.14
8	2.63	3.35	2.80	2.51	3.18	2.17
32	3.05	3.23	3.52	2.65	3.84	2.17
128	3.59	3.34	4.05	2.66	4.39	2.16
512	3.90	3.32	4.40	2.65	4.83	2.18
1024	4.00	3.34	4.54	2.68	5.06	2.19
2048	4.01	3.18	4.74	2.69	5.17	2.20
4096	4.31	3.37	4.94	2.72	5.11	2.10

Table XII—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
4	53.6	53.7	53.1	53.2
8	61.4	61.4	60.1	60.5
32	73.9	73.1	72.6	73.0
128	84.1	84.0	83.4	83.9
512	91.9	91.6	90.9	91.5
1024	93.6	93.4	93.0	94.0
2048	98.5	97.0	96.7	97.4
4096	100.0	100.0	100.0	100.0

Borax

Table XIII—Conductivity

<i>V</i>	0°	12°.5	25°	35°
16	57.99	83.76	113.54	139.83
32	64.36	92.74	125.49	154.61
128	72.87	104.81	141.72	174.52
512	78.04	112.22	152.00	187.97
1024	79.20	113.29	153.40	189.37
2048	83.45	119.55	161.23	198.31
4096	85.50	122.28	163.99	202.65

Table XIV—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
16	2.06	3.55	2.38	2.84	2.63	2.32
32	2.27	3.53	2.62	2.83	2.91	2.32
128	2.56	3.51	2.95	2.82	3.28	2.32
512	2.73	3.50	3.18	2.83	3.60	2.37
1024	2.73	3.45	3.21	2.83	3.60	2.35
2048	2.89	3.46	3.33	2.79	3.71	2.30
4096	2.94	3.44	3.34	2.73	3.87	2.36

Table XV—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
16	67.8	68.5	69.2	69.0
32	75.3	75.8	76.5	76.3
128	85.3	85.7	86.4	86.1
512	91.3	91.8	92.7	92.7
1024	92.7	92.6	93.5	93.4
2048	97.6	97.8	98.3	97.8
4096	100.0	100.0	100.0	100.0

Potassium Acetate

Table XVI—Conductivity

V	0°	12°.5	25°	35°
4	46.13	62.62	83.35	99.88
8	48.60	67.11	88.43	105.87
32	53.09	73.59	97.29	117.46
128	55.57	77.43	102.13	123.03
512	57.17	79.91	105.16	126.87
1024	58.33	81.14	106.84	129.09
2048	59.24	82.09	108.43	129.84
4096	59.06	81.89	108.65	129.90

Table XVII—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.32	2.86	1.66	2.64	1.65	1.98
8	1.48	3.05	1.71	2.55	1.74	1.97
32	1.64	3.09	1.90	2.58	2.02	2.07
128	1.75	3.15	1.98	2.54	2.09	2.05
512	1.82	3.17	2.02	2.53	2.17	2.06
1024	1.83	3.14	2.06	2.54	2.23	2.09
2048	1.83	3.09	2.11	2.57	2.14	1.97
4096	1.83	3.10	2.14	2.61	2.13	1.96

Table XVIII—Percentage Dissociation

V	0°	12°.5	25°	35°
4	77.8	76.3	76.6	76.9
8	82.0	81.8	81.3	81.5
32	89.6	89.7	89.5	90.4
128	93.7	94.4	93.9	94.7
512	96.4	97.4	96.7	97.6
1024	98.4	98.9	98.3	99.3
2048	100.0	100.0	99.7	99.9
4096	99.6	99.8	100.0	100.0

Potassium Permanganate

The strength of the mother solution was determined volumetrically by means of potassium tetroxalate.

Table XIX—Conductivity

V	0°	12°.5	25°	35°
8	59.34	80.17	104.36	124.74
32	63.75	87.13	113.70	136.05
128	66.76	91.38	119.31	142.42
512	66.46	91.14	117.90	141.49
1024	64.65	89.05	113.95	137.09
2048	63.72	86.61	110.80	133.02
4096	62.64	87.94	111.80	133.97

Table XX—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.67	2.81	1.94	2.42	2.04	1.96
32	1.87	2.93	2.13	2.45	2.24	1.97
128	1.97	2.95	2.23	2.44	2.31	1.94
512	1.97	2.96	2.14	2.35	2.36	2.00
1024	1.95	3.02	1.99	2.24	2.31	2.03
2048	1.83	2.87	1.94	2.24	2.22	2.00
4096	2.02	3.23	1.91	2.17	2.22	1.99

Table XXI—Percentage Dissociation

V	0°	12°.5	25°	35°
8	88.8	87.7	87.5	87.6
32	95.4	95.3	95.3	95.5
128	100.0	100.0	100.0	100.0
512	99.5	99.7	98.8	99.4
1024	96.8	97.4	95.5	96.3
2048	95.4	94.8	92.9	93.4
4096	93.8	96.2	93.7	94.1

Dipotassium Phosphate

This salt was precipitated by magnesia mixture and the phosphoric acid thus determined.

Table XXII—Conductivity

V	0°	12°.5	25°	35°
2	63.01	86.82	113.04	138.16
8	79.19	109.25	143.34	174.91
32	91.69	127.42	167.61	203.80
128	102.47	142.37	188.10	230.71
512	107.76	150.85	199.40	239.84
1024	109.35	152.23	200.52	242.65
2048	110.47	157.04	206.13	242.54
4096	107.16	154.98	201.98	250.78

Table XXIII—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.91	3.03	2.10	2.42	2.51	2.22
8	2.40	3.03	2.73	2.50	3.16	2.21
32	2.86	3.05	3.22	2.53	3.62	2.16
128	3.19	3.11	3.66	2.57	4.26	2.27
512	3.45	3.20	3.88	2.57	4.04	2.03
1024	3.43	3.14	3.86	2.54	4.21	2.10
2048	3.73	3.38	3.93	2.50	3.64	1.77
4096	3.83	3.57	3.76	2.43	4.88	2.42

Table XXIV—Percentage Dissociation

V	0°	12°.5	25°	35°
2	57.0	55.3	54.8	55.1
8	71.7	69.6	69.5	69.8
32	83.0	81.1	81.3	81.3
128	92.8	90.7	91.3	92.0
512	97.6	96.1	96.7	95.7
1024	99.0	96.9	97.3	96.8
2048	100.0	100.0	100.0	96.7
4096	97.0	98.7	98.0	100.0

The group consisting of strontium acetate and magnesium bromide, nitrate, formate and acetate will be considered next.

There is nothing special to note in the case of strontium acetate. It is readily hydrolyzed, and any irregularities might easily be attributed to this fact. Attention might be called, however, to the increase in percentage dissociation with rise in temperature.

It is interesting in considering the data of the four magnesium compounds to discover, if possible, the effect of the different anions. Of course, the water of crystallization would also be a factor. This is the same, however, in the case of the bromide and nitrate, and any difference in the conductivity of these two compounds may correctly be attributed to the different anions.

On examining the data for these substances, it is readily seen that the conductivity of magnesium bromide is decidedly greater than that of magnesium nitrate. Its temperature coefficient of conductivity is also larger. This would point

to some difference in the anions either as to velocity or complexity. Apart from their remarkable similarity, magnesium acetate and formate present nothing of special interest.

Strontium Acetate

The strontium was precipitated and weighed as the carbonate.

Table XXV—Conductivity

<i>V</i>	0°	12°.5	25°	35°
2	34.94	49.26	66.52	81.11
8	56.51	80.19	106.96	129.99
32	70.69	100.20	135.25	164.88
128	81.89	117.19	157.69	193.44
512	88.50	128.09	170.16	209.22
1024	91.18	131.09	177.44	218.24
2048	97.30	139.01	180.07	219.77
4096	97.89	139.60	184.44	224.75

Table XXVI—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.15	3.29	1.38	2.80	1.46	2.20
8	1.89	3.35	2.14	2.67	2.30	2.15
32	2.36	3.34	2.80	2.79	2.96	2.19
128	2.82	3.44	3.24	2.77	3.58	2.27
512	3.17	3.58	3.37	2.63	3.91	2.30
1024	3.19	3.50	3.70	2.82	4.08	2.30
2048	3.34	3.43	3.28	2.36	3.97	2.21
4096	3.34	3.41	3.59	2.57	4.03	2.19

Table XXVII—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
2	35.7	35.3	36.1	36.1
8	57.7	57.4	58.0	57.8
32	72.2	71.8	73.4	73.4
128	83.6	83.9	85.5	86.1
512	90.4	91.7	92.3	93.1
1024	93.1	93.9	96.4	97.1
2048	99.3	99.6	97.7	97.8
4096	100.0	100.0	100.0	100.0

Magnesium Bromide

The magnesium was precipitated as ammonium magnesium phosphate, and weighed as the pyrophosphate.

Table XXVIII—Conductivity

<i>V</i>	0°	12°.5	25°	35°
2	76.34	104.05	132.92	162.25
8	93.73	130.12	170.64	206.18
32	104.56	147.24	194.42	235.51
128	113.52	159.94	211.91	257.31
512	118.93	167.72	223.06	270.40
1024	122.80	173.39	230.94	279.38
2048	127.28	179.74	238.70	289.52
4096	130.91	185.06	244.94	305.94

Table XXIX—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	2.22	2.91	2.31	2.22	2.93	2.20
8	2.91	3.11	3.24	2.49	3.55	2.08
32	3.41	3.26	3.77	2.56	4.11	2.11
128	3.71	3.27	4.16	2.60	4.54	2.14
512	3.90	3.28	4.43	2.64	4.73	2.12
1024	4.05	3.30	4.60	2.65	4.84	2.10
2048	4.20	3.30	4.72	2.63	5.08	2.13
4096	4.33	3.31	4.79	2.59	6.10	2.49

Table XXX—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
2	58.3	56.2	54.3	53.0
8	71.6	70.3	69.7	67.4
32	79.9	79.5	79.4	76.9
128	86.8	86.4	86.5	84.1
512	90.9	90.6	91.1	88.3
1024	93.9	93.7	94.3	91.3
2048	97.3	97.1	97.5	94.6
4096	100.0	100.0	100.0	100.0

Magnesium Nitrate

The magnesium was weighed as the pyrophosphate.

Table XXXI—Conductivity

<i>V</i>	0°	12°.5	25°	35°
8	88.91	123.42	160.86	191.88
32	101.55	141.97	187.10	223.24
128	110.78	155.50	204.72	247.66
512	119.01	165.77	220.89	265.33
1024	120.68	170.27	224.49	272.30
2048	123.34	173.18	229.70	280.09
4096	122.89	173.70	229.58	277.54

Table XXXII—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	2.76	3.10	2.99	2.42	3.10	1.93
32	3.23	3.18	3.61	2.54	3.61	1.93
128	3.58	3.23	3.54	2.28	4.29	2.10
512	3.74	3.14	4.41	2.66	4.44	2.01
1024	3.97	3.28	4.34	2.55	4.78	2.12
2048	3.99	3.23	4.52	2.61	5.04	2.11
4096	4.06	3.30	4.47	2.57	4.80	2.09

Table XXXIII—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
8	72.1	71.1	70.0	68.5
32	82.4	81.7	81.5	79.7
128	89.9	89.5	89.1	88.4
512	96.5	95.4	96.2	94.7
1024	97.9	98.0	99.7	97.2
2048	100.0	99.7	100.0	100.0
4096	99.7	100.0	99.96	99.1

Magnesium Formate

The magnesium was weighed as the pyrophosphate.

Table XXXIV—Conductivity

<i>V</i>	0°	12°.5	25°	35°
2	37.33	52.53	69.24	83.25
8	58.15	83.44	109.29	132.14
32	74.68	106.05	141.71	172.31
128	85.99	122.17	164.06	200.30
512	88.58	123.84	167.86	205.44
1024	94.03	133.87	176.23	209.90
2048	97.22	138.60	184.73	226.37
4096	97.18	138.74	182.91	223.19

Table XXXV—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.22	3.27	1.33	2.53	1.40	2.02
8	2.02	3.47	2.07	2.48	2.29	2.10
32	2.51	3.36	2.85	2.69	3.06	2.16
128	2.89	3.36	3.35	2.74	3.62	2.21
512	2.82	3.18	3.52	2.84	3.76	2.24
1024	3.19	3.39	3.38	2.52	3.37	1.91
2048	3.31	3.40	3.69	2.66	4.16	2.25
4096	3.32	3.42	3.53	2.54	4.03	2.20

Table XXXVI—Percentage Dissociation

V	0°	12°.5	25°	35°
2	38.4	37.9	37.5	36.8
8	59.8	60.1	59.2	58.4
32	76.8	76.4	76.7	76.1
128	88.4	88.1	88.8	88.5
512	91.1	89.3	90.9	90.7
1024	96.7	96.5	95.4	92.7
2048	99.9	99.9	100.0	100.0
4096	100.0	100.0	99.05	98.6

Magnesium Acetate

The magnesium was determined as in the preceding salt.

Table XXXVII—Conductivity

V	0°	12°.5	25°	35°
4	37.56	54.50	72.50	88.92
8	46.35	66.76	89.79	109.86
32	60.99	87.97	119.31	146.20
128	71.13	103.35	139.51	172.35
512	78.05	113.23	153.41	189.50
1024	80.38	116.73	158.95	201.71
2048	83.85	121.36	164.72	203.07
4096	84.99	121.76	165.38	203.70

Table XXXVIII—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.36	3.62	1.44	2.64	1.64	2.26
8	1.63	3.52	1.84	2.76	2.01	2.24
32	2.16	3.54	2.51	2.85	2.69	2.25
128	2.58	3.63	2.89	2.80	3.28	2.35
512	2.81	3.60	3.21	2.83	3.61	2.35
1024	2.91	3.62	3.38	2.89	4.28	2.69
2048	3.00	3.58	3.47	2.86	3.84	2.33
4096	2.94	3.46	3.49	2.87	3.83	2.32

Table XXXIX—Percentage Dissociation

V	0°	12°.5	25°	35°
4	44.2	44.8	43.8	43.7
8	54.6	54.8	54.3	53.9
32	71.8	72.2	72.1	71.8
128	83.7	84.9	84.3	84.6
512	91.9	93.0	92.8	93.0
1024	94.6	95.9	96.1	99.0
2048	98.7	99.7	99.6	99.7
4096	100.0	100.0	100.0	100.0

The next group taken up for study consists of cadmium chloride, cadmium bromide, cadmium iodide and lead chloride. Attention should be called to the fact that cadmium iodide, having no water of crystallization, has just about the same temperature coefficients of conductivity as cadmium bromide and cadmium chloride, both of which have water of crystallization. Apparent increase of percentage dissociation with rise in temperature is unusual, and is quite noticeable in the case of cadmium iodide.

Lead chloride has no water of crystallization but, like cadmium iodide, has high temperature coefficients of conductivity. There must be some factor operative here affecting temperature coefficients just as hydration does, but which, from the nature of the case, cannot be due to hydrates.

Cadmium Chloride

Silver nitrate was used to precipitate the halogen in cadmium chloride, bromide and iodide.

Table XL—Conductivity

V	0°	12°.5	25°	35°
4	33.65	46.21	60.15	71.92
8	45.32	60.85	79.30	94.59
32	65.63	90.33	118.55	142.48
128	88.34	122.98	162.32	195.71
512	106.14	148.36	197.57	236.99
1024	113.78	159.65	212.53	258.73
2048	121.19	166.23	221.36	269.00
4096	121.03	172.78	232.06	282.43

Table XLI—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.00	2.97	1.12	2.42	1.18	1.96
8	1.24	2.74	1.47	2.42	1.53	1.93
32	1.97	3.01	2.26	2.50	2.39	2.02
128	2.77	3.14	3.15	2.54	3.34	2.06
512	3.38	3.18	3.94	2.66	3.94	1.99
1024	3.67	3.23	4.23	2.65	4.62	2.17
2048	3.60	2.97	4.41	2.65	4.76	2.10
4096	4.14	3.42	4.74	2.62	5.04	2.12

Table XLII—Percentage Dissociation

V	0°	12°.5	25°	35°
4	27.8	26.7	25.9	25.5
8	37.4	35.2	34.2	33.5
32	54.2	52.3	51.1	50.5
128	72.9	71.2	69.9	69.3
512	87.6	85.9	85.1	83.9
1024	93.9	92.4	91.6	91.6
2048	100.0	96.2	95.4	95.3
4096	99.9	100.0	100.0	100.0

Cadmium Bromide

Table XLIII—Conductivity

V	0°	12°.5	25°	35°
4	28.63	40.59	53.40	64.51
8	37.80	53.36	70.44	84.81
32	57.78	82.06	109.34	132.69
128	79.77	113.57	151.23	184.16
512	101.37	143.25	190.52	232.83
1024	110.69	156.85	208.48	252.81
2048	121.23	170.89	227.41	275.22
4096	123.76	174.05	232.20	280.84

Table XLIV—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	0.96	3.35	1.02	2.51	1.11	2.07
8	1.24	3.28	1.37	2.56	1.44	2.03
32	1.94	3.35	2.18	2.66	2.34	2.14
128	2.70	3.38	3.01	2.65	3.29	2.18
512	3.55	3.30	3.78	2.64	4.23	2.22
1024	3.69	3.33	4.13	2.62	4.43	2.12
2048	3.97	3.21	4.52	2.64	4.78	2.10
4096	4.02	3.25	4.65	2.67	4.86	2.79

Table XLV—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
4	23.1	23.3	23.0	23.0
8	30.5	30.6	30.3	30.2
32	46.7	47.1	47.1	47.3
128	64.4	65.2	65.1	65.6
512	81.9	82.3	82.1	82.9
1024	89.4	90.1	89.8	90.0
2048	97.9	98.2	97.9	98.0
4096	100.0	100.0	100.0	100.0

Cadmium Iodide

Table XLVI—Conductivity

<i>V</i>	0°	12°.5	25°	35°
4	20.45	29.76	39.84	48.41
8	24.31	35.85	48.44	59.43
32	39.45	59.23	81.53	101.22
128	62.73	93.36	127.36	157.35
512	87.06	127.74	172.93	211.90
1024	96.31	140.03	188.66	231.10
2048	109.01	157.20	209.73	256.42
4096	118.78	170.69	224.93	271.27

Table XLVII—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	0.75	3.67	0.81	2.72	0.86	2.16
8	0.92	3.78	1.01	2.82	1.10	2.27
32	1.58	4.01	1.78	3.01	1.97	2.42
128	2.45	3.90	2.72	2.91	3.00	2.36
512	3.25	3.73	3.62	2.83	3.90	2.26
1024	3.57	3.71	3.82	3.71	4.24	2.25
2048	3.86	3.54	4.20	3.67	4.67	2.23
4096	4.15	3.49	4.34	2.54	4.63	2.06

Table XLVIII—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
4	17.2	17.4	17.7	17.8
8	20.5	21.0	21.5	21.9
32	33.2	34.7	36.3	37.3
128	52.8	54.7	56.6	58.0
512	73.3	74.8	76.9	78.1
1024	81.0	82.6	83.9	85.2
2048	91.7	92.1	93.3	94.5
4096	100.0	100.0	100.0	100.0

Lead Chloride

The lead was precipitated by means of sulphuric acid and weighed as lead sulphate.

Table XLIX—Conductivity

<i>V</i>	0°	12°.5	25°	35°
64	104.41	144.76	188.71	224.76
128	116.27	161.56	211.43	252.17
512	133.10	186.16	246.31	293.05
1024	136.89	191.98	253.96	306.43
2048	138.88	195.16	258.49	312.13
4096	144.70	204.36	270.26	327.80

Table L—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
64	3.23	3.09	3.52	2.43	3.61	1.91
128	3.63	3.12	3.99	2.47	4.07	1.93
512	4.25	3.19	4.81	2.58	4.67	1.90
1024	4.41	3.22	4.96	2.58	5.25	2.07
2048	4.50	3.24	5.07	2.60	5.36	2.07
4096	4.77	3.30	5.27	2.58	5.75	2.13

Table LI—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
64	72.2	70.8	69.8	68.6
128	80.4	79.0	78.2	76.9
512	92.0	91.1	91.1	89.4
1024	94.6	93.9	94.0	93.5
2048	96.0	95.5	95.6	95.2
4096	100.0	100.0	100.0	100.0

The aluminium and chromium compounds will be taken up next for discussion. In these compounds we should expect to find strong resemblances. These are very apparent. Chromium and aluminium compounds, with respect to their conductivities, are in a class by themselves. Their very large conductivities and their exceedingly large temperature coefficients must attract attention. Their very large conductivities are due mainly to the great number of ions into which they are capable of ionizing and to hydrolysis. Judging from

their water of crystallization and from freezing point lowerings,¹ they must be hydrated to an enormous extent. Their large temperature coefficients of conductivity would also indicate this to be the fact. The change in conductivity, both with rise in temperature and with dilution, is much more gradual in the case of the aluminium salts than with those of chromium. The extremely small percentage dissociation in concentrated solutions, in the case of chromium sulphate and aluminium sulphate, is worthy of notice. This is probably connected with the fact that sulphates, especially in concentrated solution, undergo marked polymerization.

Aluminium Chloride

The aluminium was determined by precipitating the hydroxide and weighing as the oxide Al_2O_3 . This was done also in the case of aluminium nitrate and aluminium sulphate.

Table LII—Conductivity

<i>V</i>	0°	12°.5	25°	35°
4	105.90	147.40	193.51	232.54
8	120.22	168.23	220.86	266.58
32	142.21	200.06	265.12	322.18
128	162.66	231.08	308.80	377.28
512	176.77	252.75	341.24	421.06
1024	184.58	266.73	360.56	446.95
2048	193.37	279.49	381.44	472.46
4096	199.03	290.06	398.79	499.92

Table LIII—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	3.32	3.14	3.69	2.50	3.90	2.02
8	3.84	3.19	4.21	2.50	4.57	2.07
32	4.63	3.26	5.21	2.60	5.71	2.15
128	5.47	3.36	6.22	2.69	6.85	2.22
512	6.08	3.07	7.08	2.80	7.98	2.34
1024	6.57	3.55	7.51	2.82	8.64	2.40
2048	6.89	3.56	8.16	2.92	9.10	2.39
4096	7.28	3.66	8.70	3.00	10.11	2.54

¹ Jones and Getman: Am. Chem. J., 31, 303 (1904). Publication No. 60, Carnegie Institution of Washington.

Table LIV—Percentage Dissociation

V	0°	12°.5	25°	35°
4	53.2	50.8	48.5	46.5
8	60.4	58.0	55.4	53.3
32	71.5	69.0	66.5	64.4
128	81.7	79.7	77.4	75.5
512	88.8	87.1	85.5	84.2
1024	92.8	91.9	90.4	89.4
2048	97.2	96.3	95.6	94.5
4096	100.0	100.0	100.0	100.0

Aluminium Nitrate

Table LV—Conductivity

V	0°	12°.5	25°	35°
4	102.82	139.22	180.52	216.54
8	115.67	158.84	206.89	248.82
32	136.32	188.54	247.70	299.96
128	156.18	217.14	287.05	349.49
512	166.97	234.81	313.05	384.43
1024	173.45	247.08	332.20	410.18
2048	179.32	255.68	345.82	428.32
4096	187.89	272.12	372.07	462.84

Table LVI—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.91	2.83	3.30	2.37	3.60	1.99
8	3.45	2.98	3.84	2.42	4.19	2.03
32	4.18	3.07	4.75	2.51	5.23	2.11
128	4.88	3.12	5.60	2.58	6.25	2.18
512	5.45	3.25	6.28	2.67	7.17	2.28
1024	5.93	3.40	6.86	2.77	7.86	2.36
2048	6.19	3.44	7.31	2.83	8.37	2.39
4096	6.90	4.53	8.19	2.95	9.32	2.45

Table LVII—Percentage Dissociation

V	0°	12°.5	25°	35°
4	54.7	51.2	48.5	46.8
8	61.6	58.4	55.6	53.8
32	72.5	69.3	66.6	64.9
128	83.1	79.8	77.1	75.6
512	88.9	86.3	84.1	83.1
1024	92.3	90.8	89.3	88.7
2048	95.4	94.0	92.9	92.6
4096	100.0	100.0	100.0	100.0

Aluminium Sulphate

Table LVIII—Conductivity

V	0°	12°.5	25°	35°
4	51.90	71.81	92.40	107.72
8	65.21	89.81	114.44	132.46
32	89.50	123.63	158.01	183.51
128	121.87	169.38	219.04	266.22
512	164.08	230.86	301.01	358.79
1024	191.95	271.31	359.16	433.51
2048	222.31	317.20	425.03	518.19
4096	262.35	378.23	514.06	634.78

Table LIX—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.59	3.06	1.65	2.30	1.53	1.66
8	1.97	3.02	1.97	2.19	1.80	1.57
32	2.73	3.05	2.75	2.23	2.55	1.61
128	3.80	3.12	3.97	2.34	4.72	2.16
512	5.34	3.25	5.61	2.43	5.78	1.79
1024	6.34	3.30	7.03	2.59	7.44	2.07
2048	7.59	3.41	8.63	2.72	9.32	2.19
4096	9.27	3.53	10.87	2.87	12.07	2.35

Table LX—Percentage Dissociation

V	0°	12°.5	25°	35°
4	19.8	19.0	18.0	17.0
8	24.9	23.7	22.3	20.9
32	34.1	32.7	30.7	28.9
128	46.5	44.8	42.6	41.9
512	62.5	61.0	58.5	56.5
1024	73.2	71.7	69.9	68.3
2048	84.7	83.9	82.7	81.6
4096	100.0	100.0	100.0	100.0

Chromium Chloride

The chromium was weighed as the oxide Cr_2O_3 in the case of both chromium chloride and chromium sulphate.

Table LXI—Conductivity

<i>V</i>	0°	12°.5	25°	35°
4	86.30	116.97	153.32	199.10
8	104.53	138.83	184.18	243.55
32	130.03	182.75	245.00	319.15
128	162.34	231.28	313.45	393.62
512	188.46	272.50	372.34	465.10
1024	200.21	294.55	403.58	504.31
2048	214.48	316.60	434.36	543.02
4096	229.73	341.14	467.61	580.16

Table LXII—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.45	2.84	2.91	2.49	4.58	2.99
8	2.74	2.62	3.63	2.62	5.94	3.23
32	4.22	3.25	4.98	2.73	7.42	3.03
128	5.52	3.40	6.57	2.84	8.02	2.55
512	6.72	3.57	7.99	2.93	9.28	3.95
1024	7.54	3.77	8.72	2.96	10.07	2.50
2048	8.18	3.82	9.42	2.98	10.87	2.50
4096	8.91	3.88	10.12	2.97	11.26	2.41

Table LXIII—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
4	37.6	34.3	32.8	34.3
8	45.5	40.7	39.4	42.0
32	56.6	53.6	52.4	55.0
128	70.7	67.8	67.0	67.9
512	82.1	79.9	79.6	80.2
1024	87.2	86.4	86.3	86.9
2048	93.3	92.9	92.9	93.6
4096	100.0	100.0	100.0	100.0

Chromium Sulphate

Table LXIV—Conductivity

<i>V</i>	0°	12°.5	25°	35°
4	58.14	78.48	99.64	116.41
8	77.85	103.64	130.18	151.17
32	120.59	158.67	197.34	230.37
128	169.08	225.60	283.56	338.67
512	215.36	292.66	376.23	472.16
1024	240.48	329.96	459.83	561.76
2048	293.38	405.65	534.55	708.14
4096	313.39	445.16	598.46	808.29

Table LXV—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.63	2.80	1.69	2.15	1.68	1.69
8	2.06	2.65	2.12	2.05	2.10	1.61
32	3.05	2.54	2.46	1.55	3.30	1.67
128	4.52	2.67	4.64	2.06	5.51	1.94
512	6.18	2.87	4.69	1.60	9.59	2.55
1024	7.16	2.98	10.39	3.15	10.10	2.22
2048	8.98	3.06	10.31	2.54	17.36	3.25
4096	10.38	3.29	12.26	2.75	20.98	3.51

Table LXVI—Percentage Dissociation

V	0°	12°.5	25°	35°
4	18.4	17.6	16.6	14.4
8	24.7	23.3	21.7	18.7
32	38.2	35.6	33.0	28.5
128	53.6	50.7	47.4	41.9
512	68.3	65.7	62.8	58.5
1024	76.2	74.1	76.8	69.5
2048	93.0	91.1	89.3	87.7
4096	100.0	100.0	100.0	100.0

In the next group will be considered manganous sulphate, silver nitrate, copper sulphate and cobalt bromide. Manganous sulphate calls for no comment. The data obtained for silver nitrate are remarkably similar to those obtained for ammonium nitrate. It apparently behaves as any other ordinary, unhydrated, binary compound. It differs from ammonium nitrate in that its percentage dissociation, apparently decreasing with rise in temperature from 0° to 25°, increases somewhat at 35°.

The data for copper sulphate resemble strikingly those obtained for manganous sulphate, cadmium bromide and cadmium iodide. At ordinary temperatures manganous sulphate and copper sulphate have the same amount of water of crystallization. That their temperature coefficients should be approximately the same is not surprising; but that the temperature coefficients of cadmium chloride and cadmium bromide, crystallizing with less water, and cadmium iodide, crystallizing with no water, should be the same is surprising.

The temperature coefficients of conductivity of cobalt bromide indicate much hydration, as would be expected from its water of crystallization.

Manganous Sulphate

The manganese was weighed as the pyrophosphate.

Table LXVII—Conductivity

<i>V</i>	0°	12°.5	25°	35°
4	37.25	51.80	67.17	79.11
8	44.11	61.37	79.77	94.06
32	59.65	83.47	109.27	129.72
128	79.46	111.74	147.24	176.10
512	97.99	138.76	184.58	222.69
1024	107.12	152.31	202.94	245.72
2048	116.15	165.28	221.33	268.33
4096	124.47	177.56	238.20	289.39

Table LXVIII—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.16	3.11	1.23	2.38	1.19	1.77
8	1.38	3.13	1.47	2.40	1.43	1.79
32	1.91	3.20	2.06	2.47	2.05	1.88
128	2.58	3.25	2.84	2.54	2.89	1.96
512	3.26	3.33	3.67	2.64	3.81	2.06
1024	3.62	3.38	4.05	2.66	4.28	2.11
2048	3.93	3.38	4.48	2.71	4.70	2.12
4096	4.25	3.42	4.85	2.73	5.12	2.15

Table LXIX—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
4	29.9	29.2	28.2	27.3
8	35.4	34.6	33.5	32.5
32	47.9	47.0	45.9	44.8
128	63.8	62.9	61.8	60.8
512	78.7	78.1	77.5	76.9
1024	86.1	85.8	85.2	84.9
2048	93.3	93.1	92.9	92.7
4096	100.0	100.0	100.0	100.0

Silver Nitrate

The silver was weighed as the chloride.

Table LXX—Conductivity

<i>V</i>	0°	12°.5	25°	35°
4	51.43	70.55	91.63	109.95
8	56.01	76.68	99.80	120.37
32	61.80	85.30	111.20	133.14
128	65.79	91.06	119.14	142.67
512	69.24	94.99	125.23	148.77
2048	69.83	96.67	126.81	151.24
4096	71.03	99.03	129.68	153.32

Table LXXI—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.53	2.98	1.69	2.40	1.83	2.00
8	1.65	2.95	1.65	2.15	2.06	2.06
32	1.88	2.94	2.07	2.43	2.19	1.97
128	2.02	2.94	2.25	2.47	2.35	1.97
512	2.06	2.98	2.42	2.55	2.35	1.87
2048	2.15	3.01	2.41	2.49	2.44	1.92
4096	2.24	3.15	2.45	2.47	2.36	1.82

Table LXXII—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
4	72.4	71.3	70.6	71.7
8	78.8	77.4	76.9	78.5
32	87.0	86.2	85.7	86.8
128	92.6	92.0	91.8	93.1
512	97.4	95.9	96.5	97.0
2048	98.3	97.6	97.7	98.7
4096	100.0	100.0	100.0	100.0

Cobalt Bromide

This salt was precipitated by means of silver nitrate, and the bromine determined from the weight of silver bromide obtained.

Table LXIII—Conductivity

<i>V</i>	0°	12°.5	25°	35°
4	87.82	120.24	155.60	196.30
8	95.04	131.29	171.30	204.48
32	105.56	147.10	193.09	233.04
128	115.88	162.19	214.02	259.91
512	119.47	169.42	224.49	273.44
1024	120.80	173.38	231.56	281.16
2048	124.00	174.68	234.28	282.65
4096	125.45	177.93	236.78	289.34

Table LXXIV—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.59	2.95	2.83	2.35	4.07	2.62
8	2.90	3.05	3.20	2.44	3.32	1.94
32	3.32	3.15	3.68	2.50	4.00	2.07
128	3.71	3.20	4.15	2.56	4.59	2.15
512	4.00	3.35	4.41	2.60	4.90	2.18
1024	4.21	3.49	4.65	2.68	4.96	2.14
2048	4.05	3.27	4.77	2.73	4.84	2.07
4096	4.20	3.35	4.71	2.65	5.26	2.22

Table LXXV—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
4	70.0	67.6	65.7	67.8
8	75.7	73.8	72.3	70.7
32	84.1	82.7	81.5	80.5
128	92.3	92.0	90.4	89.8
512	95.2	95.2	94.8	94.5
1024	96.3	97.5	97.8	97.2
2048	98.8	98.2	98.9	97.7
4096	100.0	100.0	100.0	100.0

Copper Sulphate

The sulphuric acid in this salt was precipitated and weighed as barium sulphate.

Table LXXVI—Conductivity

<i>V</i>	0°	12°.5	25°	35°
2	30.06	42.12	55.11	65.15
8	42.30	59.35	77.33	91.16
32	57.24	80.53	105.64	124.94
128	76.91	108.74	143.21	170.60
512	97.88	138.92	184.97	221.08
1024	105.85	150.86	202.57	245.05
2048	113.36	161.78	217.71	264.44
4096	119.18	171.07	231.27	281.42

Table LXXVII—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	0.96	3.19	1.04	2.47	1.00	1.82
8	1.36	3.22	1.44	2.43	1.38	1.79
32	1.86	3.25	2.01	2.50	1.93	1.83
128	2.54	3.30	2.76	2.54	2.74	1.91
512	3.28	3.35	3.68	2.65	3.61	1.95
1024	3.60	3.40	4.14	2.74	4.25	2.10
2048	3.87	3.41	4.47	2.76	4.67	2.15
4096	4.15	3.48	4.82	2.82	5.02	2.17

Table LXXVIII—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
2	25.2	24.6	23.8	23.2
8	35.5	34.7	33.4	32.4
32	48.0	47.1	45.7	44.4
128	64.5	63.6	61.9	60.6
512	82.1	81.2	80.0	78.6
1024	88.8	88.2	87.6	87.1
2048	95.1	94.6	94.1	94.0
4096	100.0	100.0	100.0	100.0

The conductivity values obtained for uranyl sulphate and uranyl acetate do not agree satisfactorily with those obtained by West.¹ His solutions were evidently standardized on a different basis. It should be noticed that the temperature coefficients, in conductivity units, of uranyl sulphate decrease with rise in temperature through *V* = 512. After this dilution they increase, as in the case of the other uranyl salts. The percentage dissociation of uranyl acetate apparently

¹ Am. Chem. J., 44, 537 (1910).

increases with rise in temperature through $V = 128$. The more dilute solutions show a decrease with rise in temperature. This may be seen in the curve for uranyl acetate which follows.

Uranyl Chloride

The uranium in uranyl chloride, nitrate, sulphate and acetate was precipitated by means of ammonium hydroxide and weighed as the oxide U_3O_8 .

Table LXXIX—Conductivity

<i>V</i>	0°	12°.5	25°	35°
4	101.45	139.09	180.45	214.70
8	110.48	157.64	206.01	246.51
32	133.05	186.56	246.12	297.84
128	148.39	209.75	279.00	339.40
512	155.98	220.70	296.56	360.44
1024	161.02	231.37	311.92	383.88
2048	168.42	242.69	328.24	405.98
4096	174.98	254.22	348.16	433.68

Table LXXX—Temperature Coefficients

<i>V</i>	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	3.01	2.97	3.31	2.38	3.43	1.90
8	3.77	3.41	3.87	2.46	4.05	1.97
32	4.28	3.22	4.76	2.55	5.17	2.10
128	4.91	3.31	5.54	2.64	6.04	2.17
512	5.18	3.32	6.07	2.75	6.39	2.16
1024	5.63	3.50	6.44	2.78	7.20	2.31
2048	5.94	3.53	6.84	2.82	7.77	2.37
4096	6.34	3.62	7.52	2.96	8.55	2.46

Table LXXXI—Percentage Dissociation

<i>V</i>	0°	12°.5	25°	35°
4	58.0	54.7	51.8	49.5
8	63.1	62.0	59.2	56.8
32	76.0	73.4	70.7	68.7
128	84.8	82.5	80.2	78.2
512	89.1	86.8	85.2	83.1
1024	92.0	91.0	89.6	88.5
2048	96.3	95.5	94.3	93.6
4096	100.0	100.0	100.0	100.0

*Uranyl Nitrate**Table LXXXII—Conductivity*

V	0°	12°.5	25°	35°
4	74.91	102.01	132.91	158.84
8	83.44	114.71	150.57	181.20
32	97.22	136.35	180.64	219.38
128	110.14	153.84	207.89	254.21
512	116.33	166.65	224.95	277.35
1024	123.14	177.76	241.47	298.63
2048	128.92	187.20	255.38	317.44
4096	136.77	200.10	274.50	343.09

Table LXXXIII—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.17	2.90	2.47	2.42	2.59	1.95
8	2.50	3.00	3.07	2.68	3.06	2.03
32	3.13	3.22	3.54	2.60	3.87	2.14
128	3.66	3.32	4.16	2.67	4.63	2.23
512	4.03	3.47	4.66	2.80	5.24	2.33
1024	4.37	3.55	5.10	2.87	5.72	2.37
2048	4.66	3.62	5.46	2.92	6.21	2.43
4096	5.07	3.71	5.95	2.97	6.86	2.50

Table LXXXIV—Percentage Dissociation

V	0°	12°.5	25°	35°
4	54.8	51.0	48.4	46.3
8	61.0	57.3	54.9	52.8
32	71.1	68.1	65.8	63.9
128	80.5	77.9	75.8	74.1
512	85.0	83.3	82.0	80.8
1024	90.0	88.8	88.0	87.1
2048	94.2	93.6	93.1	92.5
4096	100.0	100.0	100.0	100.0

*Uranyl Sulphate**Table LXXXV—Conductivity*

V	0°	12°.5	25°	35°
8	78.13	99.77	120.82	136.43
32	100.65	129.52	156.80	176.52
128	128.62	166.72	203.02	229.42
512	157.54	207.90	257.69	295.20
1024	175.68	235.28	296.95	343.01
2048	191.68	260.77	332.57	391.00
4096	203.33	285.05	373.65	446.33

Table LXXXVI—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.73	2.22	1.68	1.68	1.56	1.29
32	2.31	2.30	2.18	1.68	1.97	1.26
128	3.05	2.37	2.90	1.74	2.64	1.30
512	4.03	2.56	3.98	1.91	3.75	1.46
1024	4.77	2.72	4.93	2.10	4.61	1.55
2048	5.53	2.89	5.74	2.20	5.84	1.76
4096	6.54	3.22	7.09	2.49	7.27	1.95

Table LXXXVII—Percentage Dissociation

V	0°	12°.5	25°	35°
8	38.4	35.0	32.3	30.6
32	49.5	45.4	42.0	39.6
128	63.2	58.5	54.3	51.4
512	77.5	72.9	69.0	66.2
1024	86.4	82.5	79.5	76.9
2048	94.2	91.5	89.0	87.6
4096	100.0	100.0	100.0	100.0

Uranyl Acetate

Table LXXXVIII—Conductivity

V	0°	12°.5	25°	35°
8	30.59	42.75	56.53	68.12
32	39.65	55.08	72.25	86.67
128	51.48	70.66	91.34	108.52
512	63.57	86.06	110.47	129.06
1024	70.13	94.74	120.37	141.12
2048	76.81	103.65	131.78	154.46
4096	83.75	113.81	145.10	170.54

Table LXXXIX—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.97	3.12	1.10	2.57	1.16	2.05
32	1.23	3.10	1.37	2.49	1.44	1.99
128	1.53	2.97	1.65	2.34	1.72	1.88
512	1.80	2.83	1.95	2.26	1.86	1.68
1024	1.97	2.81	2.05	2.16	2.08	1.73
2048	2.15	2.80	2.25	2.17	2.27	1.72
4096	2.41	2.88	2.50	2.20	2.54	1.75

Table XC—Percentage Dissociation

V	0°	12°.5	25°	35°
8	36.5	37.6	39.0	40.0
32	47.3	48.4	48.8	50.8
128	61.5	62.1	63.0	63.7
512	75.9	75.6	76.1	75.7
1024	83.7	83.3	83.0	82.8
2048	91.7	91.1	90.8	90.6
4096	100.0	100.0	100.0	100.0

FIGURES

So far little or nothing has been said in regard to the percentage dissociation of the salts studied. Attention will be called to these by means of curves. The curves of ten of the thirty salts showed the percentage dissociation to be almost a linear function of rise in temperature. Plotting percentage dissociation as ordinates against rise in temperature as abscissae, for each dilution, in ten cases out of the thirty, curves were obtained resembling the one for aluminium sulphate, Fig. I. The other 20 salts all showed variations in the maxima or minima. Some of these are very slight. Diagrams of the most striking variations follow. The salts giving curves showing the percentage dissociation to be a linear function of rise in temperature were acid ammonium sulphate, aluminium nitrate, aluminium chloride, aluminium sulphate, uranyl chloride, uranyl sulphate, uranyl nitrate, chromium sulphate, cadmium chloride and manganous sulphate. The others showed more or less variations, the most striking being here represented.

Fig. II is very interesting, showing in the case of cadmium iodide the increase in percentage dissociation with rise of temperature from $V = 8$ to $V = 2048$.

From the curve, Fig. III, it is easily seen that the percentage dissociation of chromium chloride increases decidedly with rise in temperature between 25° and 35° . The increase becomes less and less as the dilution increases.

Uranyl acetate shows an increase in percentage dissociation in the more concentrated solutions, but at greater dilutions gives a falling curve (Fig. IV).

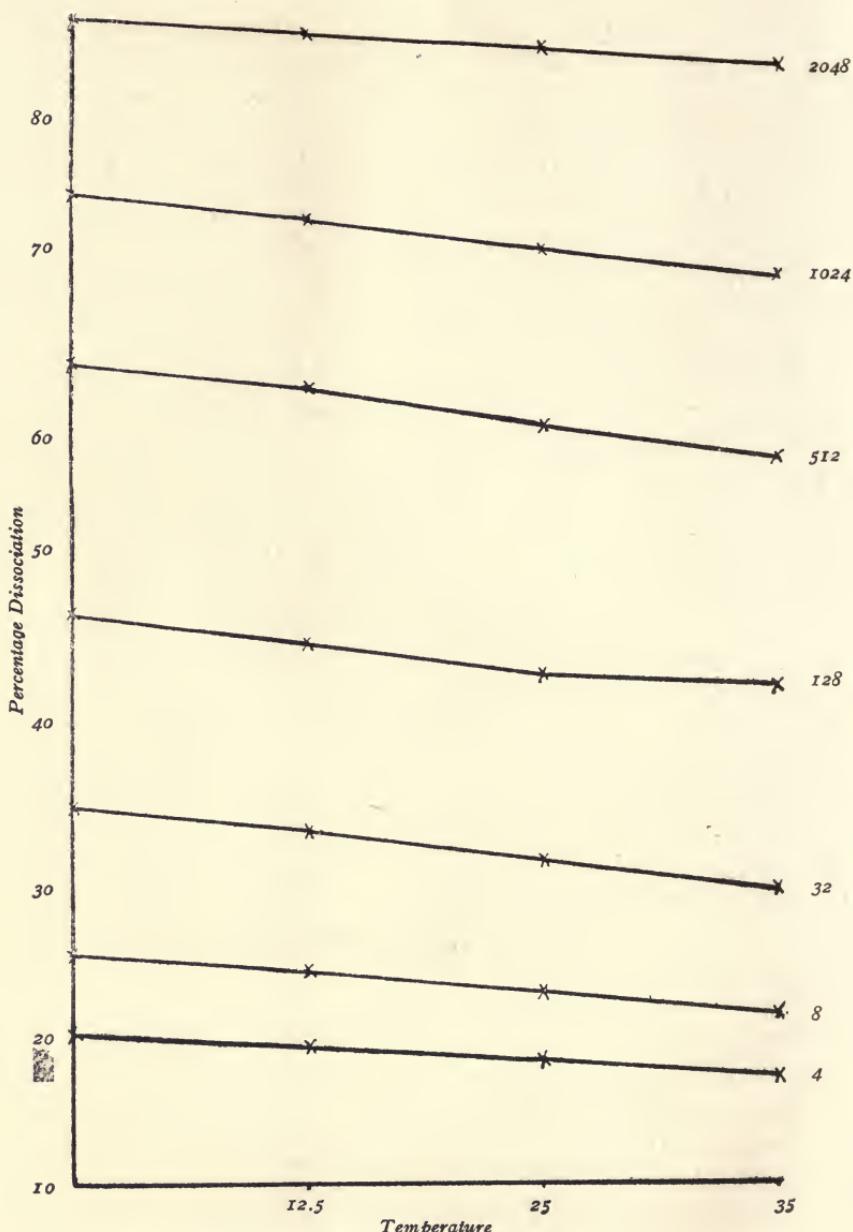


Fig. I—Aluminium Sulphate

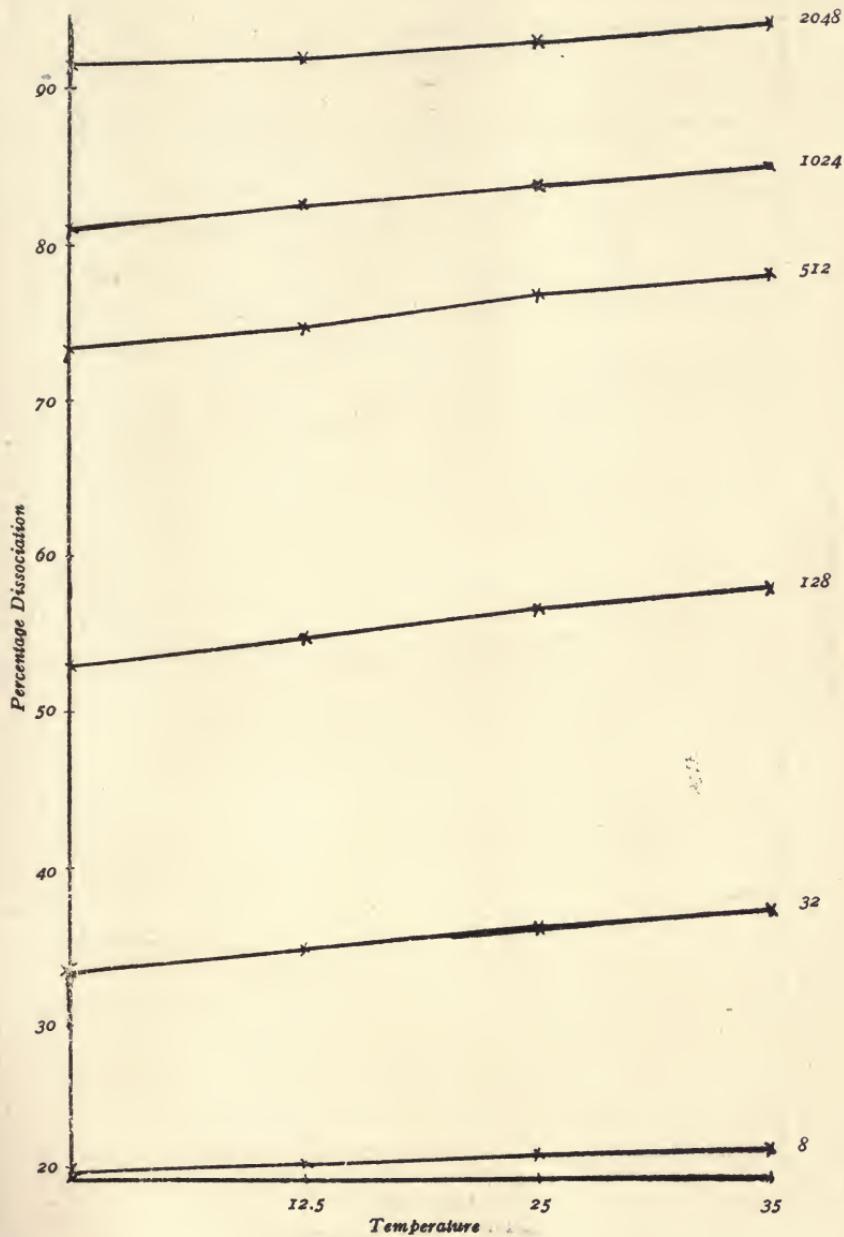


Fig. II—Cadmium Iodide

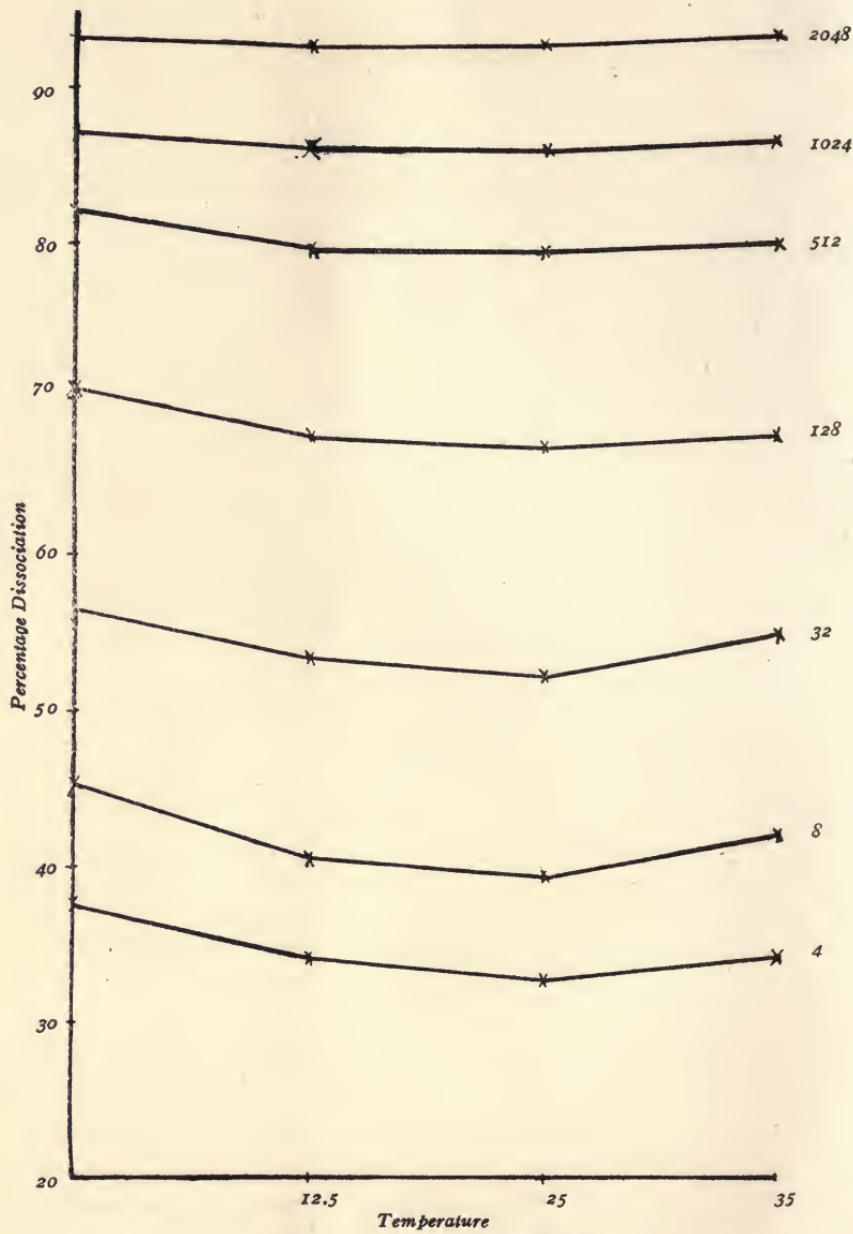


Fig. III—Chromium Chloride

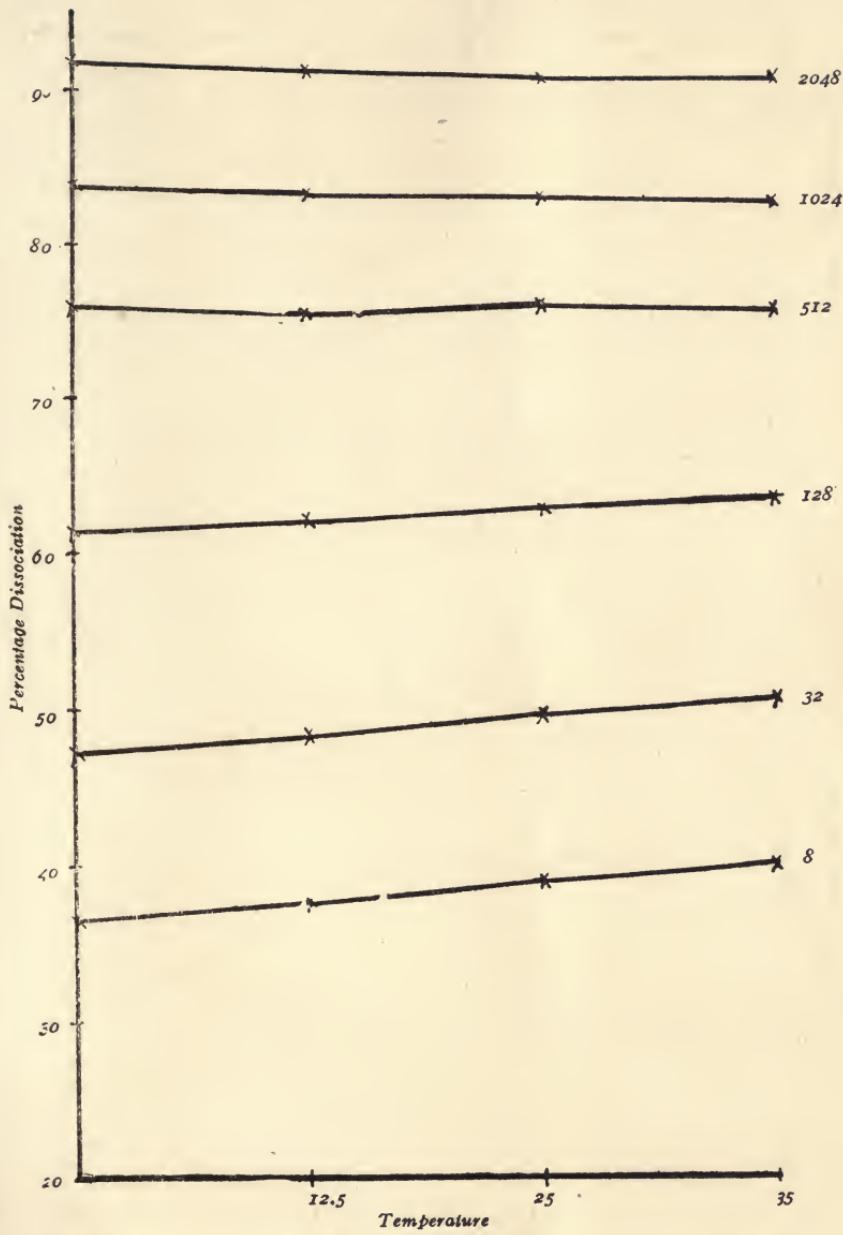
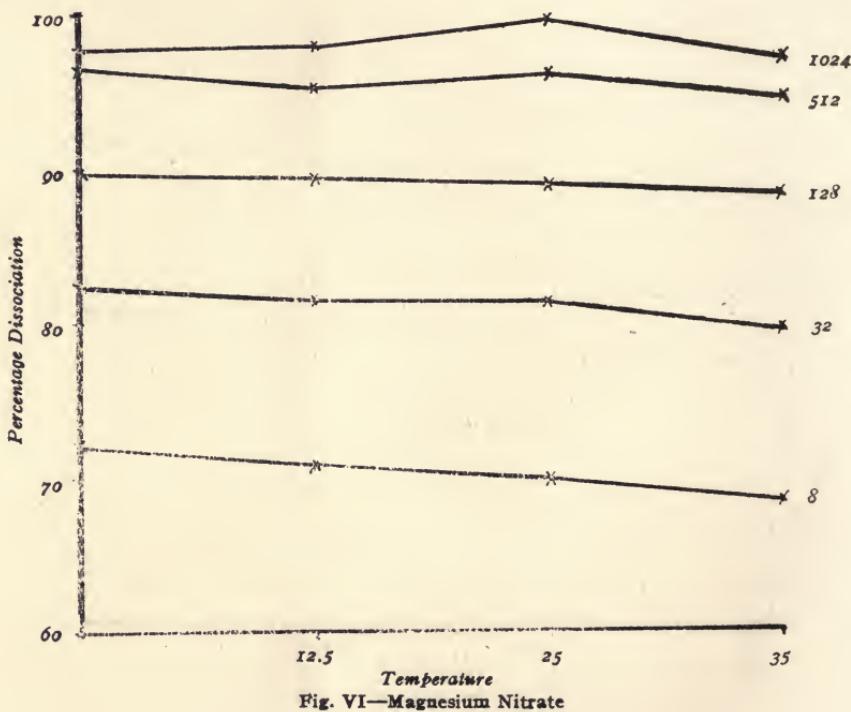
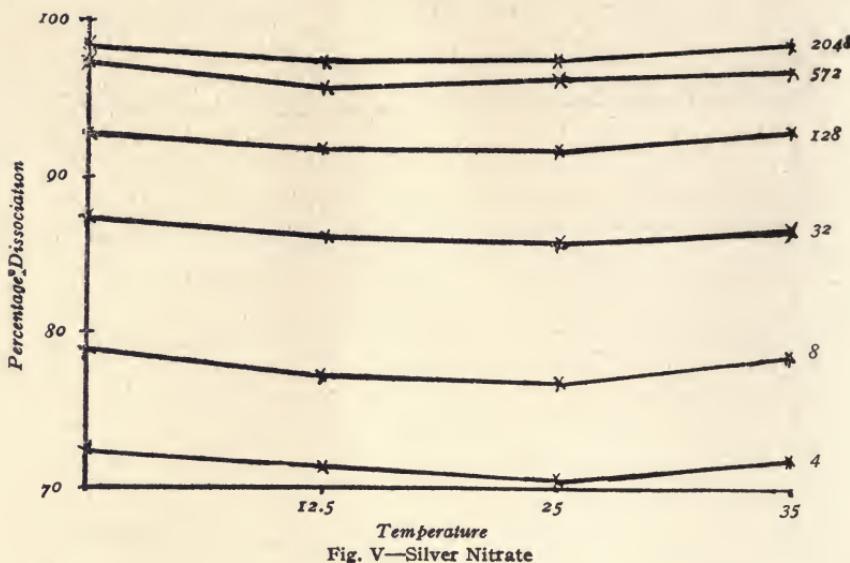


Fig. IV—Uranyl Acetate



Silver nitrate shows a decided increase in percentage dissociation with rise in temperature from $V = 4$ to $V = 2048$. See Fig. V.

The curves representing magnesium nitrate and magnesium bromide (Figs. VI and VII) show a remarkable resemblance. The maxima at higher dilutions are pronounced.

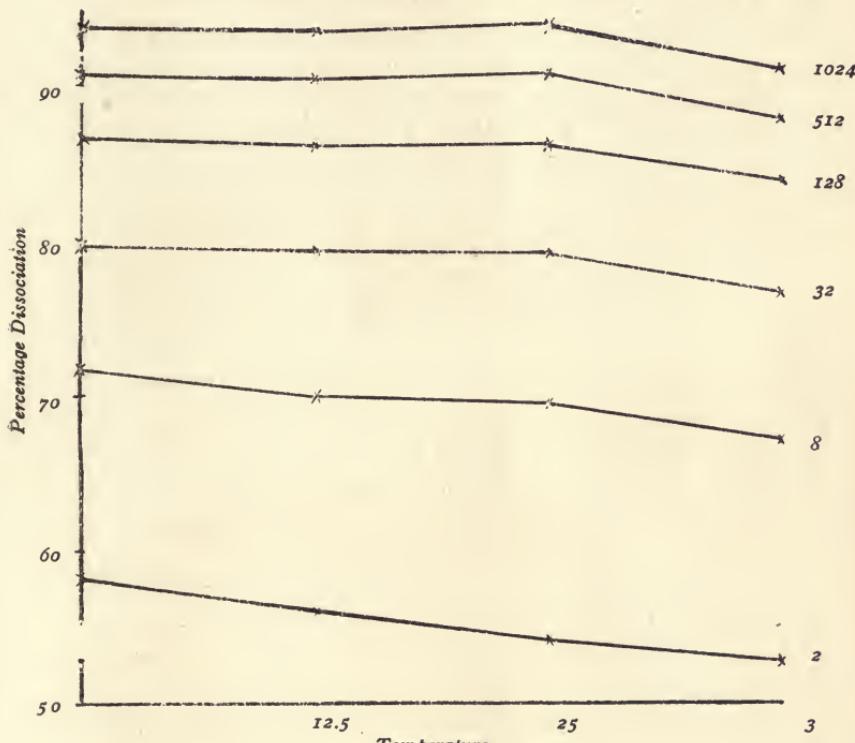


Fig. VII—Magnesium Bromide

An examination of the curves raised the question, what produces this variation? The apparent increase in percentage dissociation with rise in temperature would, naturally, be thought to be due to hydration. When there is little or no hydration the question becomes more difficult to answer. If, however, the ions are assumed to be complex, rise in temperature would bring about greater dissociation, and the effect

would be just the same as if hydrates had been present. It is difficult to differentiate the two factors. That hydrates exist is not doubted. The complexity of the ions is not so well established, so that we shall present arguments only for the latter. If the change were a gradual increase, it might be attributed easily to hydration, but a change from an increase to a decrease in dissociation could not be accounted for in this way; whereas complex ions once dissociated might reach a state where recombination would take place. Moreover, the amount of hydration has been found to depend on the amount of water of crystallization. In several of the preceding salts, notably in the case of cadmium compounds, cadmium iodide, which has no water of crystallization, is found to have temperature coefficients of conductivity equal in magnitude to those of cadmium chloride, cadmium bromide and copper sulphate, all of which have water of crystallization. Lead chloride, also, which has no water of crystallization, has temperature coefficients which compare well with those of substances that are much hydrated, i. e., copper sulphate and cobalt bromide. This would indicate that there must be some other factor present producing the same effect as hydration.

SUMMARY

1. In the main the results obtained in the case of the thirty salts studied tend to confirm the earlier results.
2. Without exception conductivity increases with rise in temperature and with dilution.
3. The temperature coefficients of conductivity expressed in conductivity units, with two exceptions, increase with rise in temperature, while the temperature coefficients expressed in percentage decrease.
4. Salts greatly hydrated have large temperature coefficients. The amount of hydration, judged by the temperature coefficients, seems closely related to the water of crystallization.
5. The apparent exceptions to the results earlier obtained, viz., an increase in percentage dissociation with rise in temperature and a large temperature coefficient when there is no

reason to expect large hydration, point, in the opinion of the author, strongly to the view advanced above, that inductive action takes place through the solvent between charged ions and neutral molecules, and that this gives rise to complex molecules and ions in solution.

After sufficient work has been done in this field, it is hoped to bring together all of the conductivity and dissociation data obtained in this laboratory and to publish them as a monograph. However, before this is done it is intended to repeat the work with every substance, where the repetition is not already completed starting with new material, repurifying, restandardizing and remeasuring the conductivity.

Work will be continued in this laboratory along the lines indicated above, probably for at least the next ten years, and there will be six investigators working here in this field during the next academic year.

BIOGRAPHY

Lula Gaines Winston, the author of this dissertation, is a daughter of Professor Charles H. Winston, LL.D., of Richmond College, Virginia. Having graduated at the Richmond High School, she entered Richmond College and received the degree of B.S. in 1899.

Since that time she has attended the Harvard Summer School for three years, taking courses in Chemistry and Physics.

During the session 1901-1902, she was teacher of Science in the Richmond Female Seminary. In 1902 she was elected teacher of Chemistry and Physics in the State Female Normal School, Farmville, Virginia, which position she still holds, having been given leave of absence for the past two years to pursue her studies at Johns Hopkins University.

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